Bi surfactant effects on ordering in GaInP grown by organometallic vapor-phase epitaxy

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The effect of the isoelectronic surfactant Bi on surface structure and ordering has been studied for GaInP semiconductor alloys grown by organometallic vapor-phase epitaxy. A small amount of Bi (trimethylbismuth) added during growth is found to result in disordering for layers grown using conditions that would otherwise produce highly ordered materials. An order of magnitude increase in the step velocity was observed by atomic-force microscopy. Bi completely eliminates three-dimensional islands on the singular (001) surface. © *2000 American Institute of Physics.* [S0003-6951(00)03919-X]

CuPt atomic-scale ordering occurs in $Ga_{0.52}In_{0.48}P$ layers grown by organometallic vapor-phase epitaxy (OMVPE) on (001)-oriented GaAs substrates.[1,2] The Ga and In atoms spontaneously segregate into alternating {111} monolayers to produce alloys having the CuPt ordered structure. Although CuPt ordering is commonly observed in ternary and quaternary compound semiconductors, it is not the stable structure in the bulk.[3] Theoretically, the alternating surface stresses resulting from the formation of [110] rows of $[\bar{1}10]$-oriented phosphorous dimers on the (2×4)-like reconstructed (001) surface thermodynamically stabilize the variants of the CuPt structure with ordering on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes.[1–3]

The driving force for ordering is understood, as described above, but the mechanism remains unknown even though several speculative models have been proposed.[4] Besides the known role of surface reconstruction, surface steps may also play an important role in the ordering process. For example, [110] steps are observed to assist the ordering.[5] This indicates that kinetic effects at step edges affect the ordering process under certain growth conditions. Indeed, ordering is closely connected with the surface structure, and thus it provides useful fingerprints by which surface processes occurring during growth can be traced and studied.

Ordering in semiconductor alloys is of considerable practical interest because CuPt ordering has a large effect on the material properties. For example, the band gap is found to be 160 meV lower in partially ordered $Ga_{0.52}In_{0.48}P$ than in disordered material of the same composition.[6] This may be used for the fabrication of heterostructures and quantum wells with no change in solid composition at the interface, resulting in fewer defects. Control of ordering is also important for solar cells,[7] visible light-emitting diodes[8] and visible laser diodes.[9]

Surfactants, surface-active substances, accumulate at the surface and alter the surface properties of materials.[10] Generally, an element with a low solubility and a low vapor pressure is likely to build up on the surface, since it is rejected from the lattice, but does not evaporate. Surfactant effects related to the surface structure have been the object of study in both elemental[11,12] and III/V semiconductors.[13,14] Sb has been shown to destroy the ordering in SiGe alloys by changing the surface reconstruction during molecular-beam epitaxy growth.[15] The surfactant Bi, also a donor in the elemental semiconductors, has been used to produce atomically abrupt Si/Ge/Si heterointerfaces.[16] In addition, Bi has been reported to alter the surface structure of Si, resulting in a $(2\times n)$Bi–Si(001) reconstruction with second-layer Bi dimers.[17] In III/V semiconductors, Bi has been shown to modify the surface morphology of wurtzite GaN films.[18] The isoelectronic surfactant Sb has also been shown to result in the modulation of the band-gap energy of GaInP grown by OMVPE by changing the order parameter.[19]

The purpose of this work is to show that a small amount of Bi added during OMVPE growth has a marked effect on the order parameter of GaInP. A very low concentration of Bi added during growth destroys the ordering and leads to a large change in step velocity, as measured by atomic-force microscopy (AFM). The effect of the surfactant Bi on the step velocity is comparable to that found for Te in a previous work.[20] The effect of Bi on GaInP provides useful information for understanding the ordering occurring at the surface during epitaxial growth. Bi is isoelectronic with P, thus this work raises the possibility of using Bi to control the band-gap energy, independent of the Fermi-level position, as demonstrated previously for Sb in GaInP.[19] The effects of the surfactants Bi and Sb are compared in this letter.

$Ga_{0.52}In_{0.48}P$ layers were grown in a horizontal, infrared-heated, atmospheric-pressure OMVPE system on semi-insulating GaAs substrates with GaAs buffer layers as described previously.[20] Both singular (001) and vicinal 3°_{B} [misoriented 3° toward the (111) B direction] substrate orientations were used. The substrates were prepared by standard degreasing followed by a 1 min etch in a $12H_2O{:}2NH_4OH{:}1H_2O_2$ solution. They were then rinsed for 5 min in deionized water and blown dry with filtered N_2 gas before being loaded into the reactor. Trimethylgallium at −7.2 °C and trimethyllndium at 25.4 °C were used as the group-III precursors. Phosphine (PH_3) was used as the group-V precursor. Trimethylbismuth (TMBi) at −7.2 °C was used as the Bi precursor. All of the layers were grown at

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620 °C with a V/III ratio of 80 and a total flow rate of 4400 ml/min. The growth rate was approximately 0.96 μm/h. An undoped, ordered GaInP layer approximately 0.16 μm thick was grown followed by the thick ($\sim$0.32 μm) GaInP layer grown with TMBi. In order to obtain sufficiently low Bi concentrations, a reduced duty cycle for the TMBi flow was used (for example, 20 s of TMBi flow out of every 60 s of growth). The solid composition of the GaInP was determined from x-ray diffraction using Vegard's law. All samples were confirmed to have a mismatch of $<0.1\%$.

Photoluminescence (PL) measurements were performed at 20 K. The 488 nm line of an Ar^+ laser with a power of 10 mW focused to a 0.5 mm^2 spot was used to excite the samples. The PL signal was dispersed with a SPEX monochromator and detected with a photomultipller tube using standard lock-in amplifier techniques.

After growth of the GaInP layers, the samples were quickly cooled to room temperature in a PH_3 and H_2 ambient in order to maintain the step structure of the surface formed during growth. The step structure was characterized using a Nanoscope III atomic-force microscope in tapping mode. The average step spacing for the entire sample was obtained from a careful counting of the average step spacing along ten, 1 μm AFM profiles.

Room-temperature Hall-effect measurements were performed on ordered, undoped, GaInP layers and disordered layers produced by the addition of TMBi during growth. All of the GaInP layers were *n* type. The carrier concentrations in the layers produced with Bi were slightly lower than for the undoped layers. The addition of Bi during growth does not appreciably change the Fermi level of GaInP.

Secondary-ion-mass spectroscopy (SIMS) depth profiles of GaInP layers grown with the addition of Bi were performed by Applied Microanalysis Laboratories. Bi in the layers was below the detection limit ($<1\times10^{15}\,cm^{-3}$) of the SIMS system. However, a significant amount of Bi was observed on the surface. This clearly indicates that Bi is a surfactant in GaInP.

Figure 1(b) shows the PL spectrum for an ordered $Ga_{0.52}In_{0.48}P$ layer grown on a singular substrate without Bi. Figure 1(a) shows the PL spectrum for a layer grown with the addition of TMBi, i.e., Bi/III ratio of 1.2×10^{-2} in the vapor phase. The PL spectra for $Ga_{0.52}In_{0.48}P$ layers grown with and without TMBi on a vicinal (3°_B) substrate are shown in Figs. 1(c) and 1(d), respectively. The peak energies for the undoped layer and the layer with Bi are 1966.5 and 1854.7 meV, respectively. This indicates that the layers grown without Bi are highly ordered, but the layers are essentially disordered when grown with Bi present. The 112 meV difference in the band-gap energies for layers grown on vicinal substrates with and without Bi shows the large change in degree of CuPt ordering between the layers. The change in PL peak energy is clearly not due to alloying, since the amount of Bi in the solid is minute.

The addition of the surfactant Sb during growth to control the ordering and, thus, the band-gap energy of GaInP layers has been used to produce heterostructures.[19] Bi has also been used to grow disorder-on-order heterostructures. The disordered layer, produced by adding TMBi, was grown on the undoped, ordered GaInP layer without interruption.

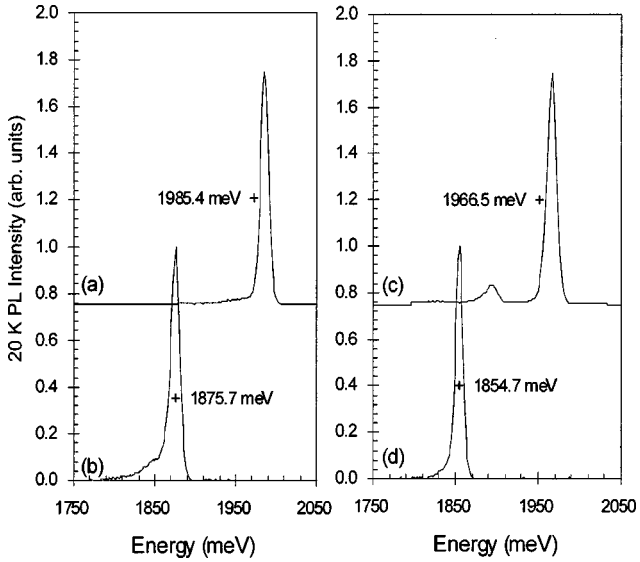

FIG. 1. 20 K PL spectra for GaInP grown on singular (001) GaAs substrates with (a) (Bi/III)$v=1.2\times10^{-2}$ and (b) without TMBi; and for layers grown on 3°_A-misoriented GaAs substrates with (c) (Bi/III)$v=1.2\times10^{-2}$ and (d) without TMBi.

Figure 1(c) shows the PL spectrum for a disorder-on-order heterostructure grown by this procedure. A 70 meV difference in band-gap energy between the two layers was achieved. This demonstrates the potential of the surfactant Bi for the production of atomically engineered structures for advanced electronic and photonic devices. The ability to independently modulate the band gap and the Fermi-level position, since Bi is isoelectronic with P, is the key to the potential usefulness of this technique.

Figure 2 shows AFM images for an undoped GaInP layer [Fig. 2(a)] and for layers grown with TMBi on singular (001) substrates with Bi/III ratios in the vapor of 5.5×10^{-3} (b), and 1.65×10^{-2} (c). Figure 2 demonstrates the dramatic change in surface morphology caused by adding TMBi during growth. The average step spacing indicates that the [110] step velocity increases by an order of magnitude as the Bi/III ratio is increased from 0 to 1.65×10^{-2}. The AFM images also show that the three-dimensional island structure observed in the layer without Bi is completely eliminated by the addition of TMBi during OMVPE growth. Bi reduces the rms roughness from a value of 0.533 nm in the layer without Bi to 0.233 nm for the layer with a Bi/III ratio in the vapor of 0.0165.

These results are in some ways similar to results obtained for Te-doped GaInP.[20,21] The addition of Te during

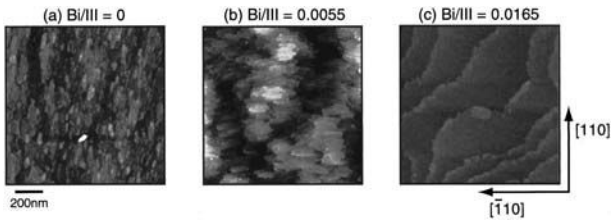

FIG. 2. AFM images vs the Bi/III ratio in the vapor phase for GaInP layers grown on singular (001) GaAs substrates. (a), (b), and (c) are for Bi/III values of 0, 5.5×10^{-3}, and 1.65×10^{-2}, respectively. Note that the surface is smoothed by the addition of Bi during growth. Each image is 1000 nm$\times$1000 nm.

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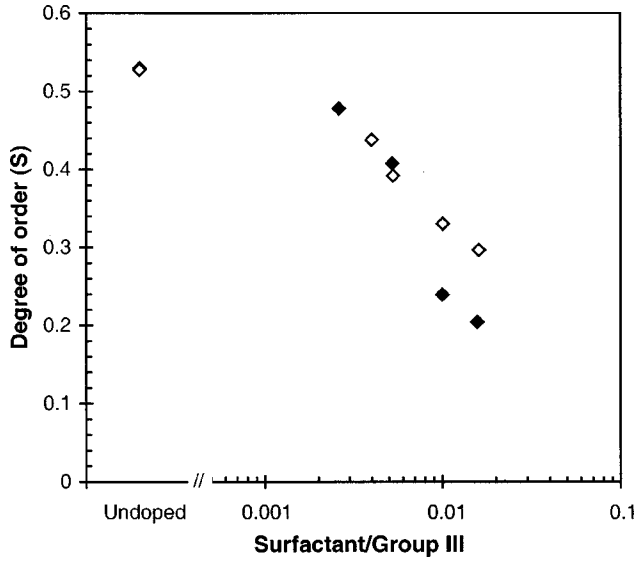

FIG. 3. Order parameter vs surfactant to group-III ratio, for Bi(♦) and Sb(◇). The ability of Bi to control the order parameter is comparable to the results for Sb. The surfactant Bi produces disordered GaInP at approximately the same concentration as required for the surfactant Sb.

GaInP growth also produces a marked change in the step structure. The $[\bar{1}10]$ step velocity increases by over an order of magnitude with increasing doping level, leading directly to the loss of CuPt ordering. However, the addition of Bi increases the [110] step velocity by an order of magnitude. The donor Te apparently affects the adatom attachment kinetics at the $[\bar{1}10]$ steps;[22] whereas, Bi affects the adatom attachment at the [110] steps.

Figure 3 shows a plot of the order parameter versus surfactant to group-III ratio in the vapor phase. The low-temperature PL peak energy was used to determine the degree of order S using the following equation:[23]

$$\text{Degree of order } (S) = \sqrt{\frac{2005 - \text{PL peak energy at 20 K (in meV)}}{471}},$$

where 2005 meV is the band-gap energy of completely disordered GaInP and 471 meV is the maximum change in the band-gap energy for perfectly ordered GaInP.

The undoped layer is highly ordered and the degree of order decreases as the surfactant to group-III ratio is increased. The lowest-order parameter (S) was achieved for a Bi/III ratio of 1.65×10^{-2}. In order to compare the results for Bi with those obtained using the surfactant Sb, the order parameter versus Sb/III ratio[24] is also plotted. Note that disordering occurs at approximately the same concentration of Bi as for Sb. The ability to control the band-gap energy of GaInP by simply modulating the TMBi flow rate is similar to the results for the surfactant Sb. An examination of the GaInP:Sb surface by AFM showed that Sb does not change the surface morphology significantly over the same range of Sb/III ratios.[25] The step velocity increases slightly with increasing TMSb flow while the root-mean-square roughness decreases, indicating some surface smoothing by the addition of Sb during growth, but less than that produced by Bi.

In conclusion, the addition of small amounts of Bi, from the pyrolysis of TMBi, during the OMVPE growth of $Ga_{0.52}In_{0.48}P$ essentially eliminates the CuPt ordering observed in layers grown without Bi. The loss of ordering leads to a 112 meV increase in the band-gap energy, as measured from the 20 K PL peak energies. These results indicate that modulation of the TMBi flow rate can be used to control the GaInP band-gap energy. The AFM images show that the [110] step velocity increases by an order of magnitude when sufficient Bi is present during growth. Bi completely eliminates three-dimensional islands on the (001) GaInP surface.

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